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#### (54) INK COMPOSITION FOR INK JET RECORDING

(71)We, DAI NIPPON TORYO CO. LTD., a Japanese Body Corporate of No. 6-1-124 Nishikujo, Konohana-ku, Osaka, Japan, and MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD., a Japanese Body Corporate, of No. 1006 Oaza Kadoma, Kadoma-shi, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to an improved ink composition for ink jet recording, which is used for an ink jet recording apparatus for performing recording by jetting ink drops in response to electric signals to cause the ink to adhere onto a recording medium.

In order for an ink for ink jet recording to be jetted in drops stably at high speeds, the ink should have the following properties at ambient temperatures:

- Viscosity: lower than 5 cps
- Surface tension: 40-50 dyne/cm
- Amount of dissolved air: not more than 0.013 ml/ml

Inks disclosed in the specifications of U.S. Patent No. 3,846,141 and British ' Patent No. 1,378,894 satisfy the requirements for the viscosity and surface tension among the above three requirements. Namely, in an ink comprising water, a water-soluble wetting agent and a water-soluble dye, an ink comprising a water-soluble solvent in addition to the foregoing basic components and an ink further comprising a minute amount of a surface active agent, it is possible to reduce the viscosity below 5 cps and adjust the surface tension to 40-50 dyne/cm. However, in conventional ink compositions for ink jet recording, no adjustment of the amount of dissolved air is made. If the

amount of dissolved air is too large, an increase in the jetting pressure cannot be precisely transferred through the ink, and therefore, it becomes difficult to perform recording precisely in response to electric

The present invention relates to an ink composition for ink jet recording which can be jetted stably in drops at a high speed.

More specifically, the present invention relates to an ink composition for ink jet recording which comprises one or more than one water-soluble wetting agent, water, one or more than one water-soluble dye and an oxygen absorber (as hereinafter defined), and which at ambient temperatures contains not more than 0.013 ml/ml of dissolved air and has a viscosity lower than 5 cps and a surface tension of 40 to 50 dynes/cm.

By the term "oxygen absorber" as used herein is meant a substance which is capable of chemically reacting with oxygen, which is soluble in the ink and which does not form precipitates in the ink.

In order that the invention may be more fully, understood, preferred embodiments thereof will now be described with reference to the accompanying drawings in which:

Figure 1 is a diagram illustrating an ink jet recording apparatus in which the ink composition of the present invention can be used;

Figure 2 is a graph illustrating the relationship between the amount of dissolved air in an ink and the standing time, which is observed when the ink from which dissolved air has been removed by a degasification treatment such as boiling is allowed to stand in air;

Figure 3 is a graph illustrating the relationship between the amount of dissolved air in an ink and the threshold voltage of a recording head; and

Figure 4 is a diagram illustrating an ink 90



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vessel composed of a plastic film which is used for intercepting air from an ink.

Various apparatuses have been known for ink jet recording, and the ink composition of the present invention can be applied to these known apparatuses. An instance of such ink jet recording apparatus will now be described by reference to Figure 1.

Referring now to Figure 1, a recording head 1 comprises a piezo-electric element 2, a vibrating plate 3 and an ink chamber 10. An ink 8 held in an ink vessel 7 is fed into the ink chamber 10 through an ink feed pipe 6 and the ink chamber 10 is filled with the ink 8. Reference numerals 4 and 5 represent a nozzle and an ink drop, respectively. The recording medium 9 is composed of paper, cloth, or wood.

In the recording apparatus having the above structure, when an electric signal 11 is applied between the piezo-electric element 2 and the vibrating plate 3, the piezo-electric element 2 causes vibrations in response to the applied electric signal to increase the pressure in the ink 8 contained in the ink chamber 10. By this pressure increase, the ink 8 is jetted from the nozzle 4 in the form of liquid drops 5, and the jetted ink drops 5 adhere onto the surface of the recording medium 9 to form thereon an image corresponding to the electric signal. This ink jet recording apparatus is detailed in the specifications of U.S. Patent No. 3,747,120 and U.S. Patent No. 3,940,773.

In an ink jet recording apparatus of this type, for example, in order to record an original image having an A-4 size and a resolving degree of 6 lines per cm for 2 minutes, it is necessary for the recording head 1 to stably jet ink drops 5 in response to electric signals corresponding to image signals having a frequency lower than 10 KHz. For attaining this feature, repeated increase of the pressure by vibrations of the piezo-electric element 2 must be faithfully transferred through the ink 8.

When the ink used has a high viscosity, the resistance is enhanced on the wall surface of the ink chamber or the nozzle portion to cause pressure loss and hence, faithful transfer of the pressure is impossible. The influence of the surface tension of the ink on jetting of the ink is not serious, but too high a surface tension, of course, must be avoided. If the surface tension of the ink is too low, running of the ink takes place on the recording medium.

In the case where the amount of dissolved air in the ink is large, the higher the frequency of repetition of increase of the pressure, the more the ink comes to have properties as a compressible fluid and

the more the transfer of increase of the 65 pressure is delayed.

As is seen from the foregoing illustration, when the viscosity of the ink is high or the amount of dissolved air is large, it is impossible to transfer the increase of the pressure faithfully and as a result, it is impossible to perform recording faithfully in response to electric signals.

For the reasons set forth above, in order to jet ink drops stably at a high speed under the abovementioned recording conditions, an ink to be used for ink jet recording must satisfy the following requirements concerning physical properties at ambient temperatures:

Viscosity: lower than 5 cps Surface tension: 40—50 dyne/cm

Amount of dissolved air: not more than 0.013 ml/mi

It is a primary object of the present invention to provide an ink composition for ink jet recording, in which the foregoing requirements are sufficiently satisfied and especially in which the amount of dissolved air can be maintained at a very low level.

In general, the solubility of air in water is 0.0183 ml/ml as measured at 20°C and one atmosphere, and it is known that this water solubility consists of a solubility of oxygen which is 0.0064 ml/ml and a solubility of nitrogen which is 0.0119 ml/ml.

We measured the solubility of air in an ink composition comprising water, a watersoluble wetting agent, a water-soluble dye and a water-soluble solvent and satisfying the foregoing requirements of the viscosity and surface tension, and as a result, it was found that the solubility of air in such ink composition is substantially equal to the solubility in water.

As a result of our experiments, it was confirmed that when ink jet recording is carried out by using a recording head as shown in Figure 1, if the amount of dissolved air is larger than 0.013 ml/ml, the 110 response characteristic of the recording head is degraded.

When the driving voltage of the recording head exceeds 250 Vpp, air bubbles are readily sucked in the head from the nozzle and jetting of the ink particles becomes unstable. As will be apparent from Figure 3 illustrating the influence of the amount of dissolved air in the ink on the minimum driving voltage (threshold voltage) for jetting of the ink particles, as the amount of dissolved air increases, in order to jet the ink particles, it is necessary to raise the driving voltage, and if the amount of the dissolved air exceeds 0.013 ml/ml, the threshold voltage for jetting of the ink particles is higher than 250 Vpp and

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it becomes impossible to perform recording stably.

When an ink composition satisfying the foregoing requirements for viscosity and surface tension was subjected to a degasification treatment such as boiling so that the requirement for the amount of dissolved air was satisfied and the degasified ink composition was allowed to stand in the ink jet recording apparatus shown in Figure 1, it was found that the amount of dissolved air in the ink composition increased with the lapse of time as shown in Figure 2 and the amount of dissolved air in the ink composition was as large as 0.013 ml/ml after the lapse of about 1 hour.

Some of us previously proposed an ink vessel as shown in Figure 4 as means for eliminating the above disadvantage. Referring to Figure 4, in an ink protection vessel 7a having a vent hole 13, air is shut out from an ink 8 by a plastic film bag 12.

Resins having a low gas permeability, such as vinylidene chloride-vinyl chloride copolymers, vinylidene chlorideacrylonitrile copolymers, polyvinylidene chloride-coated nylon resins and polyvinylidene chloride-coated polyester resins, are preferably employed for formation of the plastic film bag 12. For example, when a vinylidene chloride-vinyl chloride copolymer (Krehalon, Registered Trade Mark), which is one of the materials having a lower gas permeability among those mentioned, was shaped into a film having a thickness of 40  $\mu$  and the film was used as the film bag 12, the amount of dissolved air increased at a rate of about 0.002 ml/ml/day, and in case of an ink composition formed by removing an oxygen absorber from an ink composition of Example 3 given hereinafter, the life of the ink composition was prolonged by about I week.

However, no plastic material is capable of completely shutting out gases, and such prolongation of the ink life is of no significance from the practical viewpoint.

From the experimental results shown in Figure 2, we found that the critical lower value of the amount of air dissolved in an ink is substantially equal to the solubility of nitrogen of dissolved air in the ink and the influence of dissolved air can be substantially eliminated if dissolved oxygen is removed from dissolved air. It was also found that this can be accomplished by removing oxygen which is continually being dissolved in the ink.

This removal of dissolved oxygen, in general, may be accomplished by a physical method or chemical method. According to the former physical method, oxygen is removed by boiling or pressure reduction,

but it is difficult to perform the treatment continuously and maintain the intended effect for a long time according to this physical method. Therefore, we conducted research on a chemical method for removal of dissolved oxygen, and as a result, we found that dissolved oxygen can be effectively removed without any harmful influence on the quality of an ink by incorporation of a specific oxygen absorber. Based on this finding, we have now completed the present invention.

In the present invention, a substance capable of chemically reacting with oxygen dissolved in an ink is used as an oxygen absorber. As such substance, there can be mentioned various compounds, for example, sulfites such as sodium sulfite, ammonium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite and ammonium hydrogensulfite, polyhydric phenols such as pyrogallol, and other reducing agents such as sodium trithionite and hydrazine. However, in order for these substances to be effectively used in the present invention, they must satisfy various requirements. For example, they must be easily soluble in an ink, they must not change the color of the ink, they must not generate nitrogen gas by reaction with oxygen, and they must not form precipitates. In view of these requirements, sulfites such as sodium sulfite, ammonium sulfite, potassium sulfite, sodium hydrogensulfite, potassium hydrogensulfite and ammonium hydrogensulfite are most preferred as oxygen absorbers. For example, when sodium sulfite is used as the oxygen absorber, it absorbs oxygen according to the following reaction:

# $2Na_2SO_3+O_2=2Na_2SO_4$ (formula 1)

When water, a polyhydric alcohol as a water-soluble wetting agent, a watersoluble dye and sodium sulfite are placed in an ink vessel of a vinylidene chloride-vinyl chloride copolymer as shown in Figure 4, the amount of air permeating the film vessel is 0.002 ml/ml/day and the portion accounted for oxygen is 0.0007 ml/ml/day. 115 Accordingly, the amount of sodium sulfite in the ink composition necessary for absorbing the thus dissolved oxygen is 7.9×10<sup>-6</sup> g/ml/day. In order to maintain the amount of dissolved oxygen in the ink 120 composition at a level of 0.0007 ml/ml, sodium sulfite must be incorporated into the ink composition in an amount of about 0.5% by weight. In some ink compositions, this critical concentration of sodium sulfite 125 is higher than 0.5% by weight. In an ink composition containing sodium sulfite in an

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amount larger than the above critical value, the amount of oxygen dissolved in the ink composition is maintained at a very low level and this effect is manifested until all of sodium sulfite incorporated is consumed. For example, if sodium sulfite is incorporated in an amount of 1% by weight, the life of the ink is about 630 days. However, if the amount of sodium sulfite incorporated exceeds 10% by weight, the ink is readily dried to cause clogging of the nozzle.

The water-soluble wetting agent that is used in the present invention includes polyhydric alcohols which are liquid at ambient temperatures, such as glycerin, ethylene glycol, polyethylene glycol, propylene glycol, methyl glucoside, trimethylolpropane, trimethylolethane, neopentyl glycol, sorbitol and mannitol, alkyl ethers of aliphatic polyhydric alcohols, which are liquid at ambient temperatures, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, ethoxy glycol, monopropylene glycol methyl ether, dipropylene glycol methyl ether and tripropylene glycol methyl ether, mono-acetates of alkyl ethers of aliphatic polyhydric alcohols, which are liquid at ambient temperatures, such as ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate and diethylene glycol monoethyl ether acetate, hydroxy-alkyl formamides which have 1 to 4 carbon atoms in the alkyl group, and N-vinyl-2-pyrrolidone oligomers which are liquid at ambient temperatures.

These water-soluble wetting agents may be used singly or in the form of mixtures of two or more of them.

The above-mentioned N-vinvl-2pyrrolidone oligomers can be synthesized by adding concentrated sulfuric acid as a catalyst in an amount of 0.05 to 5% by weight based on the N-vinyl-2-pyrrolidone monomer in the state diluted with substantially the same amount of acetic acid and perform oligomerization at 10 to 100°C in a solvent such as benzene.

In the present invention, a water-soluble organic solvent is incorporated in the ink composition according to need. As such solvent, there are preferably employed dioxane, acetone, diacetone alcohol, alcohols having 1 to 3 carbon atoms, dimethylformamide, pyridine, dimethylsulfoxide and N-methyl-2pyrrolidone.

Any of water-soluble dyes having such property that color change or formation of precipitates is not caused by incorporation of an oxygen absorber such as mentioned above can be used in the present invention. For example, there are employed C. I. Direct Blue 236, C. I. Direct Blue 203, C. I. Direct Blue 202, C. I. Direct Blue 15, C. I. Acid Blue 7, C. I. Acid Blue 9, C. I. Acid Yellow 1, C. I. Direct Red 227, C. I. Direct Red 225, C. I. Acid Red 87, C. I. Acid Red 92, C. I. Acid Red 52, C. I. Direct Black 51, Direct Deep Black (manufactured by Mitsuhishi Kasei), Chlorazol Viscose Black B450 (manufactured by ICI), Nigrosine G 140 (manufactured by ICI), Benzo Nerol VSF (manufactured by Bayer) and Alcohol Mazenta (manufactured by Shirado Kagaku). These water-soluble dyes may be used singly or in the form of mixtures of two or more of them.

If necessary, a surface tension adjusting agent may be incorporated into the ink composition of the present invention. As the surface tension adjusting agent, there can be used, for example, cationic surface active agents such as sodium alkyl sulfates. anionic surface active agents such as alkyl pyridium sulfates, non-ionic surface active agents such as polyoxyethylene alkyl ethers, and amphoteric surface active agents.

Moreover, the ink composition of the present invention may further comprise a viscosity modifier according to need. As the viscosity modifier, there can be mentioned, for example, cellulose derivatives such as hydroxypropyl cellulose, carboxymethylcellulose and hydroxyethyl cellulose, and water-soluble resins such as polyvinyl alcohol, polyvinyl pyrrolidone, acrylic resins, styrene-acrylic copolymers and styrene-maleic acid copolymers.

The presence of Cu<sup>++</sup> ion as a catalyst is effective for promoting the reaction represented by the above reaction formula

The ink composition of the present invention preferably comprises 5 to 40% by weight of a water-soluble wetting agent such as mentioned above, 0.1 to 10% by weight of a water-soluble dye such as mentioned above and 0.5 to 10% by weight of an oxygen absorber such as mentioned above, with the balance being water. According to need, up to 50% by weight of water may be replaced by a water-soluble organic solvent such as mentioned above. Further, small amounts of a surface active agent, an antiseptic, a fungicide, or two or more thereof may be incorporated in the ink composition of the present invention according to need.

When the ink composition according to 125 the invention is used for ink jet recording, it is possible to jet ink drops stably at a high speed in an ink jet recording apparatus, and therefore, the applications of ink jet recording can be remarkably broadened. 130

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In order that the present invention may be more fully understood, the following Examples are given by way of illustration only. In these Examples, experiments were conducted by using the ink jet recording apparatus shown in Figure 4, but it must be noted that similar effects can be obtained by using other known ink vessels.

## Example 1

10	Composition	% by weigh
	Polyethylene glycol #300	
	(having a molecular weight of	
	about 300)	20
15	Dye, C.I. Acid Red 92	5
	Distilled Water	73
	Sodium sulfite	2

A polyoxyethylene alkyl ether type surface active agent as a surface tension adjusting agent and sodium dehydroacetate as an antiseptic mildewproofing agent were incorporated in the above composition, each being at a concentration lower than 2000 ppm. The resulting ink composition had a surface tension of 40 dyne/cm and a viscosity of 2.5 cps at room temperature

The so-prepared ink composition was placed in an ink vessel as shown in Figure 4 and used for ink jet recording. The threshold voltage as 100-150 Vpp. Even after the ink composition had been stored for 18 months, the amount of dissolved oxygen was smaller than 0.0007 ml/ml and the threshold voltage was lower than 250 Vpp. Thus, it was confirmed that the ink composition retained the original excellent jetting property (adaptability to ink jet recording) even after 18 months' storage. Further, formation of precipitates or change of the color was not observed during storage.

# Example 2

45	Composition	% by weight
	Diethylenc glycol	15
	Dye, C. I. Direct Blue 202	2
	Distilled water	82
	Sodium sulfite	1

In the same manner as in Example 1, the 50 surface tension adjusting agent and antiseptic mildewproofing agent were incorporated into the above composition. The resulting ink composition had a surface tension of 45 dyne/cm and a viscosity of 1.7 cps at room temperature.

When the ink composition was subjected to the jetting test after 18 months' storage and properties were examined in the same manner as in Example 1, results as excellent

as those obtained in Example I were similarly obtained.

#### Example 3

Composition	by weight	
Glycerin	10	65
Ethylene glycol monoethyl		
ether	10	
Dye, Direct Deep Black		
(manufactured by		
Mitsubishi Kasei)	l	70
Distilled water	77	
Sodium sulfite	2	

In the same manner as in Example 1, the surface tension adjusting agent and antiseptic mildewproofing agent were incorporated in the above composition. The resulting ink composition had a surface tension of 42 dyne/cm and a viscosity of 1.5 cps at room temperature.

In the same manner as described in Example 1, the ink composition was subjected to the jetting test after 18 months' storage and properties were examined. Obtained results were as excellent as those obtained in Example 1.

#### Example 4

Composition	% by weight	
Glycerin	20	
Dye, C. I. Acid Blue 9	2.5	
Distilled water	72.5	90
Sodium sulfite	5.0	

In the same manner as in Example 1, the surface tension adjusting agent and antiseptic mildewproofing agent were incorporated into the above composition. The resulting ink composition had a surface tension of 48 dyne/cm and a viscosity of 1.8

In the same manner as described in Example 1, the ink composition was subjected to the jetting test after 18 months' storage and properties were examined. Obtained results were as excellent as those obtained in Example 1.

#### Example 5

Example 5	105
Composition % by weight	
Polyethylene glycol #300 (having a molecular weight	
(having a molecular weight	
of about 300) 14	
Diethylene glycol 25	110
Dye, C. I. Acid Blue 9 3	
Distilled water 57	
Sodium sulfite 1	

In the same manner as in Example, the surface tension adjusting agent and 115 antiseptic mildewproofing agent were incorporated into the above composition. The resulting ink composition had a surface

		- 1 - · ·	0
	tension of 40 dyne/cm and a viscosity of 2.6 cps.	Composition G % by weight	
5	tension of 40 dyne/cm and a viscosity of 2.6 cps.  In the same manner as described in Example 1, the ink composition was subjected to the jetting test after 18 months' storage and properties were examined.  Obtained results were as excellent as these	Sorbitol 3.0 Dye, Direct Red 225 1.0 Distilled water 78.0 Ammonium hydrogensulfite 3.0	60
	Obtained results were as excellent as those obtained in Example 1.	Composition H % by weight	65
10	Example 6 The following various compositions were prepared.	Glycerin 18.0 Hydroxypropyl cellulose 1.0 Dye, C. I. Direct Red 225 Distilled water 76.5 Ammonium hydrogensulfite 3.0	
15	Composition A % by weight Polyethylene glycol #600 (having a molecular weight of 600) 20.0 Dye, C. I. Direct Blue 15 1.0	Composition I % by weight Diethylene glycol monoethyl ether 10.0 Dye, C. I. Direct Blue 236 3.0 Sodium sulfite 1.0 Distilled water 86.0	70
	Dye, C. I. Direct Blue 15 1.0 Distilled water 76.0 Ammonium hydrogensulfite 3.0	Distilled water 86.0  Composition J % by weight Ethylene glycol monobutyl	75
20	Composition B % by weight 1,5-Pentane diol 17.6	ether 30.0	
	1,5-Pentane diol 17.6 Dye, C. I. Direct Red 225 Distilled water 78.4 Ammonium hydrogensulfite 3.0	Dye, C. I. Direct Red 225 Potassium sulfite Distilled water Acetone  2.0 2.0 2.0	80
25	Composition C % by weight Dipropylene glycol 12.0 Polyethylene glycol #300	Composition K % by weight Ethoxy glycol 10.0 Diethylene glycol methyl	
30	(having a molecular weight of 300) 15.0  Dye, C. I. Acid Blue 9 1.0  Distilled water 71.0	ether 5.0 Dye, C. I. Acid Blue 9 3.0 Ammonium sulfite 2.5 N-Methyl-2-pyrrolidone 3.0 Distilled water 76.5	85
	Potassium sulfite 1.0  Composition D % by weight 15.0	Composition L % by weight Ethylene glycol monoethyl	90
35	Polyethylene glycol #600	ether 15.0 Diethylene glycol monomethyl ether acetate 5.0 Dye, C. I. Acid Red 92 5.0 Potassium sulfite 1.0 Distilled water 74.0	95
40	of 40,000)  Dye, C. I. Acid Blue 9  Distilled water  Ammonium sulfite  1.0  75.0  3.0	Composition M % by weight  Ethylene glycol monoethyl ether acetate 10.0  Propylene glycol 25.0	100
45	Composition E % by weight 1,3-Butane diol 20.5	Dye, C. I. Direct Blue 15 1.0 Ammonium sulfite 3.0 Distilled water 61.0	
45	Glycerin 4.0 Polyvinyl alcohol (having a molecular weight of 500) 0.5 Due C. I. Direct Red 225	Composition N % by weight Tripropylene glycol methyl ether 15.0	105
50	Dye, C. I. Direct Red 225 Distilled water Potassium sulfite  1.0 1.0	Dye, C. I. Direct Blue 152.0Potassium sulfite7.0Distilled water76.0	110
	Composition F Diethylene glycol Sorbitol  % by weight 15.0 3.0	Composition O % by weight Diethylene glycol monobutyl ether 20.0	
55	Dye, C. I. Direct Blue 15 Distilled water Potassium sulfite  1.0 80.0 1.0	Dye, C. I. Acid Red 922.0Sodium sulfite1.0Distilled water77.0	115

	Composition P N-Vinyl-2-pyrrolidone	% by weight
	oligomer (having ar	ì
	average molecular weight	- t
5	of 300)	5.0
	Dye, C. I. Direct Blue 202	2.0
	Sodium sulfite	1.0
	Distilled water	91.0
	Ethylene glycol	1.0
10	Composition Q	% by weight
	$\beta$ -Hydroxyethyl formamide	10.0
	Dye, C. I. Direct Blue 15	2.5
	Potassium sulfite	1.0
	Distilled water	86.5
15	C ::: B	0/1
13	Composition R	% by weight
	Ethylene glycol monobutyl ether	13.0
	Glycerin	5.0
	Hydroxypropyl cellulose	
20	(HPC-SL manufactured by	, ,
	Nippon Soda)	1.0
	Dye, C. I. Direct Red 225	1.5
	Distilled water	76.5
	Ammonium hydrogensulfite	3.0
25	In the same manner as in l	Example 1, the

In the same manner as in Example 1, the surface tension adjusting agent and antiseptic mildewproofing agent were incorporated into the foregoing compositions. It was found that each of the so prepared ink compositions had a surface tension of 40—50 dyne/cm and a viscosity lower than 5 cps at room temperature.

In the same manner as described in Example 1, these ink compositions were subjected to the jetting test after 18 months' storage and properties were examined. In each ink composition, obtained results were as excellent as in Example 1.

# WHAT WE CLAIM IS:-

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1. An ink composition for ink jet recording which comprises one or more than one water-soluble wetting agent, water, one or more than one water-soluble dye, and an oxygen absorber (as hereinbefore defined), and which at ambient temperatures contains not more than 0.013 ml/ml of dissolved air and has a viscosity lower than 5 cps and a surface tension of 40 to 50 dynes/cm.

2. An ink composition according to Claim 1, comprising by weight 5 to 40% of the water-soluble wetting agent, 0.1 to 10% of the water-soluble dyes and 0.5 to 10% of the oxygen absorber, the balance being water.

3. An ink composition according to Claim 1 or Claim 2, in which the wetting agent is a polyhydric alcohol, an alkyl ether of an aliphatic polyhydric alcohol, a monoacetate of an alkyl ether of an aliphatic polyhydric alcohol, a hydroxyalkyl formamide or an N-vinyl-2-pyrrolidone oligomer.

4. An ink composition according to any one of the preceding Claims, in which oxygen absorber is sodium sulfite, potassium sulfite, ammonium sulfite, sodium hydrogensulfite, potassium hydrogensulfite, or ammonium hydrogensulfite.

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5. An ink composition according to any one of the preceding Claims which further comprises one or more than one water-soluble organic solvent which enhances the solubility of the dye in the wetting agent, one or more than one surface tension adjusting agent, one or more than one viscosity modifier, Cu<sup>++</sup> ions, one or more than one antiseptic, and/or one or more than one fungicide.

6. An ink composition substantially as herein described in any one of the Examples.

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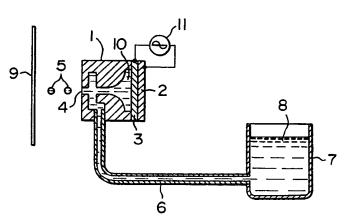


FIG.4

